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NBS TECHNICAL NOTE

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# Calculation of the Heating Value of a Sample of High Purity Methane for Use as a Reference Material

George T. Armstrong

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C., 20234.

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# TECHNICAL NOTE 299

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George T. Armstrong

Heat Division
Institute for Basic Standards
National Bureau of Standards

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# Calculation of the Heating Value of a Sample of High Purity Methane for Use as a Reference Material

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## Abstract

The heat of combustion of $CH_4$ has been recalculated in kJ $(mol)^{-1}$, Btu $(mol)^{-1}$, Btu (cu ft)$^{-1}$ (dry basis) and Btu (std. cu ft)$^{-1}$ (saturated basis), using the best available experimental determinations of the heat of combustion and other measured quantities and the most recent generally accepted physical constants and defined physical units. The calculations are outlined in detail. The resulting quantities are applied to calculation of the heat of combustion of a reference sample of $CH_4$ submitted for analysis of composition and certification of heating value by the Institute of Gas Technology.

## 1. Introduction

A former activity of the National Bureau of Standards (NBS) was to supply to industry reference samples of fuel gas, certified with respect to heat of combustion, for calibrating gas combustion calorimeters. In 1962, following a reorganization of the NBS chemistry divisions, this activity was transferred to the Institute of Gas Technology (IGT) (Illinois Institute of Technology, Chicago, Illinois). with the understanding that the NBS would periodically certify samples for use as the IGT primary laboratory reference materials.

Samples issued by the IGT are supplied with a secondary certification of the Gross- or Total-Heating Value, which is determined in their laboratory by calorimetric comparison with their primary laboratory reference material. The uncertainty limits stated by the IGT in their secondary certification are ±0.9 Btu (standard cu ft)$^{-1}$.

The heat of combustion of a sample of methane containing only small amounts of impurities can be calculated from the composition and known heats of combustion of $CH_4$ and the impurities, together with certain physical properties and conversion factors.

The most precise determination of the heat of combustion of $CH_4$ is based on the mass rather than the volume burned because of the greater accuracy with which mass can be measured. However, the users require the heat of combustion on a volume basis. In making a conversion from the precise experimental determination of the heat of combustion of pure $CH_4$ to the heat of combustion of the sample required by the users, the following factors must be taken into account:

(1) The energy unit in which the determination was made and the unit to which it must be converted.

(2) The mass unit in which the determination was made and the current accepted value of the mass unit.

(3) The temperature dependence of the heat of combustion.

(4) The current best value for the ideal molar volume of a gas.

(5) The current best value for the vapor pressure of water.

(6) The current best coefficients for the real gas behavior of methane and its mixtures with small quantities of $H_2O$ and other impurities.

(7) The analysis of the gas.

This report outlines in detail how these factors are taken into account. The results are then applied to two samples submitted by the Institute of Gas Technology and their heating values are calculated on a dry basis and on a saturated basis in Btu $(\text{cu ft})^{-1}$ at 60°F. The calculations are shown in elaborate detail because it has been our experience that annoying small discrepancies in calculations by different people can occur because of differences either in source data or in method of rounding figures. In these calculations an excessive number of figures is carried, in many instances well beyond the level of significance, in order to prevent any errors of rounding. In general each physical quantity used is treated as exact for the purpose of calculation, and rounding to a significant figure is only done at the end of the calculations.

The procedure as outlined in sections 2-12 is valid as a calculation of the heat of combustion of pure methane on a weight basis and on a volume basis, both dry and water-saturated. Because the best available value from NBS for the heat of combustion of $CH_4$ and of other measured physical quantities, and the values of general physical constants and defined units accepted by NBS have been used, the calculation of the heat of combustion may be taken as our best estimate of this quantity on the basis of current information.

The American Society for Testing and Materials (ASTM) definitions for standard cubic foot, heating value, and related quantities have been used (except where distinctions are noted) because the principal use of the gas described is as a reference gas for calibrating calorimeters following ASTM procedures [1].

2. ASTM Definitions of Terms [1].

(1) Total Calorific Value: The total calorific value (Total or Gross Heating Value) of a gas is the number of British thermal units evolved by the complete combustion, at constant pressure, of one standard cubic foot of gas with air, the temperature of the gas, air and products of combustion being 60 F, and all the water formed by the combustion reaction being condensed to the liquid state.

(2) Net Calorific Value: The net calorific value of a gas is the number of British thermal units evolved by the complete combustion, at constant pressure, of one standard cubic foot of gas with air, the temperature of the gas, air, and products of combustion being 60 F, and all of the water formed by the combustion reaction remaining in the vapor state.

(3) British Thermal Unit[a]: A British thermal unit, or Btu, is the quantity of heat that must be added to one avoirdupois pound of pure water to raise its temperature from 58.5 F to 59.5 F under standard pressure.

(4) Standard Cubic Foot of Gas: A standard cubic foot of gas is the quantity of any gas that at standard temperature and under standard pressure will fill a space of one cu. ft. when in equilibrium with liquid water.

(5) Standard Temperature: The standard temperature is 60 F, based on the International Temperature Scale.[b]

(6) Standard Pressure: The standard pressure is the absolute pressure of a column of pure mercury 30 in. in height at 32 F and under standard gravity (32.174 ft $sec^{-2}$). (See footnote (a), Section 3.0.)

(7) Saturated Basis: The expressed total calorific value of a gas when it is saturated with water at standard temperature and pressure; 1 cu. ft. of this gas is equivalent in dry gas content to 0.9826 cu. ft. of dry gas at the temperature and pressure. (See footnote (a), Section 6.0.)

---

[a] Note that the Btu as used in ASTM methods for gaseous fuels is different from that used in ASTM methods for liquid petroleum fuels and ASTM methods for coal and related solid fuels.

[b] We interpret this as the International Practical Temperature Scale of 1948, Text Revision of 1960.

## 3. Defined Quantities and Exact Equivalent Quantities

The quantities listed in Table 1 are the definitions and exact equivalents used in this report. Where inconsistencies exist between definitions of Table 1 and ASTM definitions, the definitions in Table 1 are used. Such inconsistencies are explained in footnotes to Table 1.

Table 1

| | |
|---|---|
| 1 inch = 2.54 cm (exactly) | [2] |
| 1 cubic foot = $(2.54 \times 12)^3$ = 28316.846592 $cm^3$ | |
| Standard gravitational acceleration = 980.665 cm $s^{-2}$ [a] | [2] |
| 1 standard atm. pressure = 1,013,250 dyn $cm^{-2}$ [b] | [2] |
| 1.8 deg F = 1 deg C | [2] |
| 32 °F ≙ 0 °C ≙ 273.15 °K | [2] |
| 1 int. J (NBS) = 1.000165 J | [3,4] |
| 1 lb. = 453.59237 g | [2] |
| 1 cal = 4.1840 J | [2] |

## 4. Accepted Physical Quantities

In Table 2 are listed values for the derived physical quantities whose values are not defined but are dependent upon the properties of some material.

Table 2

| | |
|---|---|
| R (gas constant) = 8.3143 ±0.0008[c] J $(deg\ K)^{-1}$ $mol^{-1}$ | [2] |
| $V_o$ (ideal gas) = $(2.24136 \pm 0.00010)^c \times 10^4$ $cm^3$ $mol^{-1}$ | [2] |

---

[a] On the basis of this definition the acceleration in ft $s^{-2}$ is 32.1740485$\bar{5}$, which differs from the value listed in definition (6) Section 2.0 by 1.5 parts in $10^6$.

[b] We take 13.595080 g $cm^{-3}$ [20] for the density of mercury at 0°C and one atm pressure, which we adjust to 13.595052 g $cm^{-3}$ at 0°C under an average pressure of 1/2 atm as is appropriate for the density of a column of mercury supported by one atm of gas pressure. The height of a column of mercury of this density supported by one atm pressure under standard gravitational acceleration is 76.000257 cm.

[c] Uncertainties in R and $V_o$ are interdependent. The uncertainties given are 2σ.

In Table 3 are listed values for thermodynamic properties of materials that were accepted for use as data in making the calculations of this Technical Note.

Table 3

| | |
|---|---|
| $C_p^o$ ($CH_4$) at 25°C = 8.439[a] cal $deg^{-1}$ $mol^{-1}$ | [19] |
| $C_p^o$ ($O_2$) at 25°C = 7.016[a] cal $deg^{-1}$ $mol^{-1}$ | [19] |
| $C_p^o$ ($CO_2$) at 25°C = 8.87 [a] cal $deg^{-1}$ $mol^{-1}$ | [19] |
| $C_p^o$ ($H_2O$) at 15°C = 4.1858 $Jg^{-1}$ $(deg\ C)^{-1}$ | [14] |
| $H_{30}^o - H_{25}^o$ ($H_2O$) = 20.8949 $Jg^{-1}$ | [14] |
| $H_{25°C}^o - H_{15.555°C}^o$($H_2O$) = 39.4962 $Jg^{-1}$ | [14] |
| P($H_2O$) at 15°C = 0.017429 atm | [5,6] |
| $\Delta H_c^o$[$CH_4$(g)] at 25°C = 212.790[a] kcal $mol^{-1}$ | [Section 9] |

## 5. Total Moles of Ideal Gas in a Cubic Foot at Standard Temperature and Standard Pressure

In the calculation below, t is the temperature in degrees above the ice point, T is the temperature in degrees K, P is the absolute pressure, R is the gas constant, V is the volume, and N is the number of moles in a cubic foot at standard temperature and standard pressure. All values are taken from Table 1 or Table 2.

$t = 60°F = 15.55555°C$

$T = 273.15 + 15.55555 = 288.70555°K$

$P = 30$ in. Hg = 762 mm Hg = 1.002628185 atm

$= 1{,}015{,}913.01$ dyn $cm^{-2}$

$$N = \frac{PV}{RT} = \frac{1{,}015{,}913.01 \times 28316.846592 \times 10^{-7}}{(8.3143 \pm .0008) \times 288.70555}$$

$= 1.198452 \pm .000115$ mol $ft^{-3}$

The uncertainty in the number of moles per cubic foot is almost solely due to the uncertainty of the gas constant R.

---

[a] See footnote Section 12.

## 6. Moles of $H_2O$ and $CH_4$ in a Cubic Foot of Ideal Gas (Saturated Basis)

Osborne and Meyers [5] report the vapor pressure of water to be 0.25592 lb $(in.)^{-2}$ at 60 F which we adjust upward by 0.00022 lb $(in.)^{-2}$ to 0.25614 lb $(in.)^{-2}$ on the basis of the difference at 15 °C between the values given by Osborne and Meyers and the later revision by Osborne, Stimson and Ginnings [6]. Using the same conversion factor, 14.6960 lb $(in.)^{-2}$ = 1 atm, as was used by Osborne and Meyers, we find for the partial pressure of $H_2O$ vapor 0.017429 atm. or 17659.93 dyne $cm^{-2}$.

The residual pressure of gas is 1,015,913.01 - 17,659.93 or 998,253.08 dyne $cm^{-2}$.[a] The water present is 0.0208330 moles and the other gas present is 1.177619 moles ±0.000114 moles. The uncertainty in the number of moles is based primarily on the uncertainty in R.

## 7. Gas Imperfection of $CH_4$

In calculating the heating value of methane, real gas, for NBS Circular 464 [7], Jessup used a value of 0.99800 ±0.00005 for the quantity PV/RT [8], at one atm pressure and 60 °F, which he obtained from unpublished calculations of C. S. Cragoe. Since then Douslin [9] has measured the P-V-T relations of methane. For the Beattie-Bridgman equation (1)

$$P = [RT\ (1-\varepsilon)/V^2][V+B] - A/V^2 \qquad (1)$$

he lists

$$A = A_o\ (1-a/V) = 2.2152\ (1-0.02174/V)$$
$$B = B_o\ (1-b/V) = 0.05159\ (1+0.02198/V)$$
$$\varepsilon = C/T^3V = 15 \times 10^4/T^3V$$

We assume that for a mixture of $CH_4$ with a small amount of $H_2O$ P (total) is appropriate for P in calculating PV/RT. We calculate V roughly from the ideal gas equation.

$$V = RT/P = (8.3143 \times 288.70555)/1,015,916.45$$
$$= 23,627.776\ cm^3$$

Next we calculate the constants A, B and ε.

$$A = 2.2152\ (0.99908) = 2.21316$$
$$B = 0.05159\ (1.000930) = 0.051638$$
$$\varepsilon = 15 \times 10^4/(288.7055)^3 \times 23.627$$
$$= 15 \times 10^4/56 \times 10^7 = 0.26 \times 10^{-3}$$

---

[a] The residual pressure leads to a factor of 0.9826167 for the ratio of moles of $CH_4$ in a cubic foot of saturated gas to moles of $CH_4$ in a cubic foot of dry gas. This differs by 17.0 parts in $10^6$ from the factor 0.9826 given in definition (7) Section 2.0.

The Beattie-Bridgman equation can be rearranged to give equation (2).

$$PV/RT = [(1-\epsilon)[V+B]/V] + A/VRT \qquad (2)$$

We are now prepared to calculate the factors and terms of equation (2).

$(1 - \epsilon) = (1 - 0.00026) = 0.99974$

$(V + B)/V = (23.627 + 0.051638)/23.627 = 1.002186$

$(1 - \epsilon)(V + B)/V = 1.001924$

$A/VRT = 2.21316/23.627 \times .082054 \times 288.7055 = 0.003954$

$PV/RT = 1.001924 - 0.003954 = 0.997970$

This value for PV/RT is within the limits 0.99800 ±0.00005 suggested by Jessup and so we retain the same uncertainty, but use our calculated value of PV/RT for PV/RT(real, saturated) and also for PV/RT(real,dry).

## 8. Moles of Methane in a Standard Cubic Foot of Real Gas (Saturated Basis) and a Cubic Foot of Dry Gas

Using symbols as defined in Section 5, but allowing N (real, saturated) now to be the number of moles of real gas in a standard cubic foot, we calculate as follows. For the saturated gas

$$N(\text{real, saturated}) \times (PV/RT)(\text{real,saturated}) = N(\text{ideal saturated})$$

$$N(\text{real,saturated}) = \frac{1.177619 \pm 0.000114}{.99797 \pm 0.00005}$$

$$= 1.180014 \pm (0.000114) \pm (0.000059)$$

$$= 1.180014 \pm .000128 \text{ moles } CH_4/(\text{standard cubic foot real gas})(\text{saturated basis}).$$

For the dry gas we similarly calculate

$$N(\text{real, dry}) \times (PV/RT)(\text{real, dry}) = N(\text{ideal, dry})$$

$$N(\text{real, dry}) = \frac{1.198452}{0.99797}$$

$$= 1.200890 \text{ moles } CH_4/(\text{cubic foot real gas})(\text{dry basis}).$$

## 9. Heating Value of Pure Methane

Prosen and Rossini reported the heat of combustion of $CH_4$ at 25°C to be -212.798 ±0.072 kcal $mol^{-1}$ [10]. This was derived from the measurements of Rossini [11], and is consistent with the values -212.80, and -212.798 kcal $mol^{-1}$ reported by Rossini and co-workers [4,13] in their compilations for the American Petroleum Institute. Rossini's determination is used in this work as the best value for the heat of combustion of methane. A detailed description of adjustment of the heating value to correspond to currently accepted physical units and standard conditions is given below.

(a) Citation of original data. The value originally reported by Rossini [11,a] at 30°C and one atm pressure of real gas, for a mole corresponding to 36.0312 grams of $H_2O$ formed was $\Delta H_c$ = -889.700 ±0.218 int. kJ (NBS) $mol^{-1}$. This was modified by Rossini [11,b] to correct for an error in reducing his conditions to one atm pressure to $\Delta H_c$ = -889.720 ±0.230 int. kJ (NBS) $mol^{-1}$.

(b) Adjustment to standard states. We assume that in the combustion as carried out by Rossini, oxygen and methane entered the calorimeter in the pure state at one atm pressure and the exit gases consisted of $H_2O$ at its vapor pressure and $CO_2$ at a sufficient pressure to make up one atm.

The enthalpy correction for non-ideality, $H^\circ - H$, is shown for these gases in Table 4 and in Figure 1 for convenience in interpolation. The data for $CO_2$ and $O_2$ are taken from Hilsenrath, et al. [17], and the data for $CH_4$ are taken from Tester [18]. The mixture of $CO_2$ with a small amount of $H_2O$ is presumed to have the same P-V-T properties as pure $CO_2$ at one atm pressure.

The enthalpy change in the ideal gas state at one atm pressure is the same as the enthalpy change of the real gases at zero pressure. The correction reactions are shown below as reactions 1-5.

$CH_4(g,p=1\ atm) + 2O_2(g,p=1\ atm) = 2H_2O(\ell) + CO_2(g,p=1\ atm)\ \Delta H_{30} = -889.720$ (1)

$CH_4(g,p=0) = CH_4(g,p=1\ atm)$ at 30°C, $\Delta H = (H - H^\circ)(CH_4) = -.0162$ (2)

$2O_2(g,p=0) = 2O_2(g,p=1\ atm)$ at 30°C, $\Delta H = (H - H^\circ)(2O_2) = -.0156$ (3)

$CO_2(g,p=1\ atm) = CO_2(g,p=0)$ at 30°C, $\Delta H = (H^\circ - H)(CO_2) = +.0418$ (4)

---

$CH_4(g,p=0) + 2O_2(g,p=0) = 2H_2O(\ell) + CO_2(g,p=0)$ $\Delta H^\circ_{30} = -889.710$ (5)

$\Delta H$ for reaction (5) is the standard heat of reaction at 30°C in int. kJ(NBS) $mol^{-1}$ for a mole equivalent to 36.0312 g $H_2O$.

(c) Adjustment to absolute Joule (abbreviation, J). As one int. J(NBS) is 1.000165 J, the value listed in eq (5) is equal to $\Delta H^{\circ}_{30}$ = -889.8568 kJ $mol^{-1}$ for a mole equivalent to 36.0312 g $H_2O$.

(d) Adjustment of atomic weights. At the time of publication of Prosen and Rossini [10] the atomic weight scale of 1941 was in use and the molecular weight of water was taken to be 18.016; the mole of methane thus corresponding then to 36.032 g $H_2O$. Converting we find $\Delta H^{\circ}_{30}$ = -889.8766 kJ $mol^{-1}$ (1941) for a mole equivalent to 36.032 g $H_2O$. At the time of the present report the atomic weight scale of 1961 [16] is in use, and the molecular weight of water is 18.01534. Converting by this number we find

$$\Delta H^{\circ}_{30} = -889.8440 \text{ kJ mol}^{-1} \text{ (1961)}$$

for a mole of $CH_4$ corresponding to 36.03068 g $H_2O$.

(e) Adjustment to 25°C. From Table 3 we find

$$(H^{\circ}_{25}-H^{\circ}_{30})(2H_2O) = -36.03068 \times 20.8949 = -752.8574 \text{ J mol}^{-1}$$

$$(H^{\circ}_{25}-H^{\circ}_{30})(CO_2) = -5 \times 4.184 \times 8.87 = -185.5604$$

$$(H^{\circ}_{30}-H^{\circ}_{25})(CH_4) = +5 \times 4.184 \times 8.439 = +176.5439$$

$$(H^{\circ}_{30}-H^{\circ}_{25})(2O_2) = +5 \times 4.184 \times 2 \times 7.016 = +293.5494$$

$$(H^{\circ}_{25}-H^{\circ}_{30})(\text{Reaction (5)}) = -468.3245 \text{ J mol}^{-1}$$

Adjusting the heat of reaction we find $\Delta H^{\circ}$ at 25°C = -890.345 kJ $mol^{-1}$ (1941) = -212.798 kcal $mol^{-1}$ (1941) based on a mole equivalent to 36.016 g $H_2O$. The latter value is the value reported by Prosen and Rossini [10], who assigned an uncertainty (twice the estimated standard deviation of the mean) of 0.072 kcal $mol^{-1}$.

On the basis of a mole equivalent to 36.03068 g $H_2O$. we find

$$\Delta H^{\circ} \text{ at } 25°C = -890.312 \pm 0.300 \text{ kJ mol}^{-1} \text{ (1961)}$$

$$= -212.790 \pm 0.072 \text{ kcal mol}^{-1} \text{ (1961)}$$

Table 4. Values of Enthalpy Functions
at One Atmosphere Pressure

| T | $O_2$ [17] | | $CO_2$ [17] | | $CH_4$ [18] | |
|---|---|---|---|---|---|---|
| | $(H^o-E_o^o)/RT_o$ | $(H-E_o^o)/RT_o$ | $(H^o-E_o^o)/RT_o$ | $(H-E_o^o)/RT_o$ | $H^o-H_o^o$ | $H-H_o^o$ |
| °K | $RT_o$ = 2271 J $mol^{-1}$ | | $RT_o$ = 2271 J $mol^{-1}$ | | cal $mol^{-1}$ | cal $mol^{-1}$ |
| 280 | 3.5875 | 3.5835 | 3.8300 | 3.808 | 2243.4 | 2238.7 |
| 290 | 3.7166 | 3.7129 | 3.9908 | 3.970 | | |
| 300 | 3.8459 | 3.8424 | 4.1537 | 4.135 | 2412.7 | 2408.7 |
| 310 | 3.9754 | 3.9721 | 4.3186 | 4.301 | | |
| 320 | | | | | 2585.5 | 2582.1 |

## 10. Adjustment of Heat of Combustion to 60°F

The reaction involved in the combustion is reaction (1)

$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(\ell) \qquad (1)$$

For this reaction

$$\Delta H_{T°C} = \Delta H_{25°C} + (H_T-H_{25})[CO_2] + (H_T-H_{25})[2H_2O(\ell)] - (H_T-H_{25})[CH_4] - (H_T-H_{25})[2O_2]$$

For $CO_2(g)$, $CH_4(g)$, and $O_2(g)$ we take $H_T-H_{25}$ to be (T-25) x $C_p$ at 25°C and calculate $H_T-H_{25}$ for $H_2O$ from enthalpy tables. Values for $C_p$ at 25°C are selected from Wagman, et al. [19], as listed in Table 2. For water we find enthalpy data by Osborne, Stimson, and Ginnings [14] at one atmosphere pressure, which has the values 104.8994 J $g^{-1}$ at 25°C and 67.2632 J $g^{-1}$ at 16°C. Using an interpolated value of $C_p$ = 4.1851 J $g^{-1}$ $deg^{-1}$ for the heat capacity of water at 15.7777°C, we calculate for the enthalpy difference $H_{16°C} - H_{15.5555°C}$ = 1.8600 J $g^{-1}$. The enthalpy difference $H_{25°C}-H_{15.5555°C}$ = 39.4962 J $g^{-1}$ (that is 104.8994 - 67.2632 + 4.1851 x 0.44444). This is equal to 711.5375 J $(mol)^{-1}$.

We tabulate below the heat capacity contributions.

| | $H_{15.5555}-H_{25}$ J |
|---|---|
| $CO_2$ | - 350.66 |
| $2H_2O(\ell)$ | -1423.09 |
| $2O_2$ | + 554.48 |
| $CH_4$ | + 333.47 |
| Reaction (1) | - 885.79 |
| Estimated uncertainty | ± 8.8 |

From above we have -0.886 ±0.0088 kJ $mol^{-1}$ for the adjustment to 60°F (15.55555°F). The standard heat of combustion at 60°F is therefore

$$\Delta H^{\circ}_{60F} = -891.196 \text{ jK mol}^{-1}{}^{a} \quad (1961 \text{ basis})$$

with an uncertainty of 0.300 kJ $mol^{01}$.

We now make the adjustment to real gases at 60°F. The reactions given below indicate the changes required to reduce the combustion energy from that of the ideal gas reaction to that of the real gas reaction at 60°F. The data for reactions (2'), (3') and (4') are taken from Figure 1.

| | $\Delta H^{\circ}$ at 60°F | |
|---|---|---|
| $CH_4(g,p=0) + 2O_2(g,p=0) = 2H_2O(\ell) + CO_2(g,p=0)$ | -891.196 kJ $mol^{-1}$ | (1') |
| $CH_4(g,p=1 \text{ atm}) = CH_4(g,p=0)$ $(H^{\circ}-H)(CH_4)$ | = .0183 | (2') |
| $2O_2(g,p=1 \text{ atm}) = 2O_2(g,p=0)$ $(H^{\circ}-H)(2O_2)$ | = .0172 | (3') |
| $CO_2(g,p=0) = CO_2(g,p=1 \text{ atm})$ $(H-H^{\circ})(CO_2)$ | = .0470 | (4') |
| $CH_4(g,p=1 \text{ atm}) + 2O_2(g,p=1 \text{ atm}) = 2H_2O(\ell) + CO_2(g,p=1 \text{ atm})$ | -891.2075 | (5') |

11. Value of the British Thermal Unit (Btu)

From definition (3), the specific heat of water from Osborne, Stimson, and Ginnings [14], and constants from Table 1, we calculate 1 Btu to be 1054.803 ±0.08 J $(lb)^{-1}$ $(deg\ F)^{-1}$ in the following way. The heat capacity $C_p$ of water at 59°F (15°C) is 4.1858 J $g^{-1}$ $(deg\ C)^{-1}$ and between 14°C and 16°C deviates from this in an approximately linear way, so that the average heat capacity from 58.5°F to 59.5°F can be taken as the heat capacity at 59°F.

[a] See footnote Section 12.

The value of the Btu is, therefore:

$$1 \text{ Btu} = [4.1858 \times 453.59237/1.8]$$
$$= 1054.804 \text{ J}$$
$$\pm 0.08 \text{ J}$$

An uncertainty of 0.0003 J $g^{-1}$ (deg C)$^{-1}$ is assigned to the heat capacity of water at this temperature on the basis that W. J. de Haas selected 4.1855 J $g^{-1}$ (deg C)$^{-1}$ for the best value of the heat capacity of water (see Stimson [15]). This is equivalent to an uncertainty of 0.08 J in the Btu as defined in Section 2. Note that this uncertainty applies only to the British thermal unit as defined above. Other definitions of the Btu may lead to values differing by larger amounts.

## 12. Heat of Combustion of $CH_4$ in Btu per cubic foot

Using figures previously calculated, we evaluate the heat of combustion of $CH_4$ as listed below.

The heat of combustion in Btu (mol)$^{-1}$ is

$$\Delta H^{o}_{c60F}(CH_4) = -891.2075/1054.804 = -844.9034 \text{ Btu (mol)}^{-1}$$

with an uncertainty of (0.286 + .0084 + 0.071 Btu $mol^{-1}$) = 0.295 Btu $mol^{-1}$.

The heat of combustion in Btu per cubic foot is

$$\Delta H^{o}_{c60F}(CH_4)(\text{dry basis}) = 1.200890 \times 844.9034 = 1014.636 \text{ Btu (cu ft)}^{-1}$$

$$\Delta H^{o}_{c60F}(CH_4)(\text{saturated basis}) = 1.180014 \times 844.9034$$
$$= 996.998^{a} \text{ Btu (std cu ft)}^{-1}$$

The fractional uncertainty in the heat of combustion of pure methane is

$$\sqrt{\left(\frac{0.295}{844.9}\right)^2 + \left(\frac{0.000128}{1.180014}\right)^2} = \sqrt{(0.000350)^2 + (0.000108)^2} = \sqrt{13.4 \times 10^{-8}}$$

$$= 3.65 \times 10^{-4} = .0365 \text{ percent or } 0.360 \text{ Btu (std cu ft)}^{-1}$$

---

[a] The value listed here differs slightly but not significantly from a value informally reported previously. The difference is due to (a) a slight change in heat capacities accepted for the reaction components, and (b) a slight difference in the corrections to the molar heat of reaction for non-ideality of gases at 30°C and at 15.5555°C.

13. Analysis of Two Special Methane Samples for Certification

Cylinder No. 58156 and No. 20608T of methane supplied by the Matheson Company, were submitted by the Institute of Gas Technology for analysis for certification. The analyses were performed by E. E. Hughes of the Analysis and Purification Section, of the NBS Analytical Chemistry Division. The report of analysis forms Appendix I. The two cylinders of gas were of the same composition so far as could be determined, and therefore only one analysis was submitted. The analysis indicates that the samples were as pure as or purer than that used by Rossini [11] in his experimental determination of the heat of combustion of $CH_4$.

In Table 5 we give the analysis used in the calculation together with the uncertainty in the mole fraction of each component and the heat of combustion of each component.

Table 5

Composition of Gas Samples Submitted for Certification

| Component | Mole Fraction | Uncertainty | $\Delta H_c$ Btu (std cu ft)$^{-1}$ | |
|---|---|---|---|---|
| $CH_4$ | 0.999521 | 0.000201 | 997.001 | |
| $C_2H_6$ | .000400 | .000200 | 1758. | [7] |
| $N_2$ | .000017 | .000004 | 0.0 | |
| $O_2$ | .000002 | .000002 | 0.0 | |
| $CO_2$ | .000060 | .000020 | 0.0 | |

## 14. Heat of Combustion of the Two Special Samples

Only one heat of combustion was calculated for the two samples. It was calculated from equation (2), in which

$$\Delta H_c(CH_4 \text{ sample}) = \Delta H_c(CH_4) \times n(CH_4) + \Delta H_c(C_2H_6) \times n(C_2H_6) + \Delta H_c(\text{inerts}) \times n(\text{inerts}) \qquad (2)$$

Each term is the contribution of a component to the heating value, and is obtained as the product of the heating value of the component times its mole fraction. Oxygen, nitrogen and carbon dioxide are treated as inert, having zero heat of combustion.

The heat of combustion of the samples is therefore:

$$(0.999521)(1014.636) + (0.000400)(1789.0) = 1014.150 + 0.716 = 1014.866$$

Btu $(\text{cu ft})^{-1}$ (dry basis).

$$(0.999521)(996.998) + (0.000400)(1758.0) = 996.520 + 0.703 = 997.223$$

Btu $(\text{standard cu ft})^{-1}$ (saturated basis).

The uncertainty in the heat of combustion of the sample is based on the uncertainty in the heat of combustion of pure $CH_4$, and on the uncertainties in the amounts of $CH_4$ and $C_2H_6$. The uncertainty in the heat of combustion of pure $C_2H_6$ does not make a significant contribution to the uncertainty of the heat of combustion of the sample, because of the small amount of $C_2H_6$ present. The uncertainty in the heat of combustion of the sample due to the uncertainty in its composition is

$$\Delta(U_c)(\text{sample}) = \Delta H_c(CH_4) \times \Delta n(CH_4) + \Delta H_c(C_2H_6) \times \Delta n(C_2H_6)$$

We take the uncertainty in the mole fraction of $CH_4$, $\Delta n(CH_4)$, to be the square root of the sum of the squares of the uncertainties in the mole fractions of all the impurities. Since the major contribution to the uncertainty in $CH_4$ is due to the uncertainty in $C_2H_6$, $\Delta n(C_2H_6)$ will be of opposite sign from $\Delta n(CH_4)$.

The uncertainty in the heat of combustion of the sample due to uncertainty in composition is therefore:

$$-996.998 \times 0.000201 + 1758 \times 0.000200$$
$$= \pm(-.200 + 0.352) = \pm 0.152 \text{ Btu } (\text{std cu ft})^{-1}$$

The combined uncertainty in heat of combustion of the sample due to uncertainty in composition and uncertainty in heat of combustion of methane is $\sqrt{(0.360)^2 + (0.152)^2}$

$$= \sqrt{.153} = 0.391 \text{ Btu (std cu ft)}^{-1}$$

We have attempted to estimate errors in such a way that the true heat of combustion of the sample will fall within the bounds set by the error limits with a 95 percent probability.

## 15. Certificate Values for Heat of Combustion of Special Samples of Methane

In the foregoing calculations an excessive number of figures has been carried in order to avoid rounding errors. Rounding to the nearest 0.1 Btu $(\text{cu ft})^{-1}$ we therefore report for the heats of combustion of the samples submitted:

Dry Basis: 1014.9 Btu $(\text{cu ft})^{-1}$

Saturated Basis: 997.2 Btu $(\text{standard cu ft})^{-1}$

with an uncertainty (95% confidence limits) of 0.4 Btu $(\text{cu ft})^{-1}$.

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FORM NBS-348
(4-6-64)

APPENDIX I.

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D.C. 20234

# NATIONAL BUREAU OF STANDARDS
# REPORT OF ANALYSIS

June 18, 1965

of

Two Cylinders of Methane*

Submitted by G. T. Armstrong, 221.02
Proj. 2210627, Div. Req. 221-2330
Ref: Institute of Gas Technology
Test No. 185179

The contents of each cylinder were examined both by mass spectrometric and gas chromatographic techniques. Only those substances listed below were detected and the remainder of each sample is considered to be methane. The composition of each sample was identical within the stated limits and the composition given below can be considered that of either cylinder.

| | Mole Percent |
|---|---|
| Ethane | 0.04 ± 0.02 |
| Nitrogen | 0.0017 ± 0.0004 |
| Oxygen | 0.0002 ± 0.0002 |
| Carbon dioxide | 0.006 ± 0.002 |

The limit shown is a conservative intuitive guess as to the certainty of the value of the concentration. It is based on uncertainty in the measurement of chromatographic peak areas, ion currents, conversion factors, and general experience with the two methods of analysis.

E. E. Hughes, Chemist

John K. Taylor, Chief
Analysis and Purification
Analytical Chemistry Division

65-423

*Cylinder Nos. 58156 and 20608T

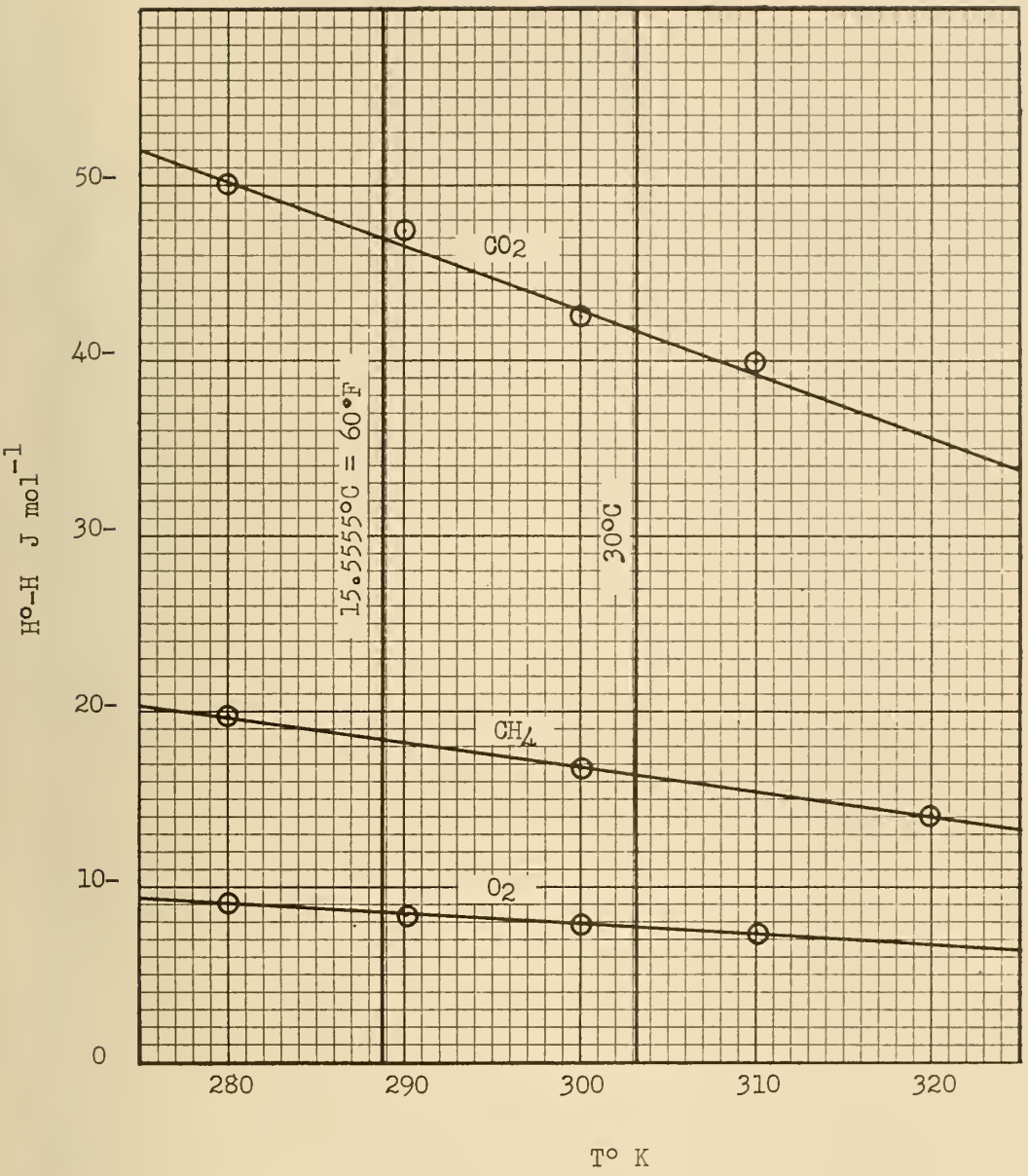


Figure 1. $H^\circ - H$ for combustion gases at p = one atmosphere pressure

Sources of Data

$O_2$ and $CO_2$: NBS Circ. 564 [17]

$CH_4$: H. E. Tester [18]



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